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EFFECT OF PRESSURE ON THE DISSOCIATION OF ELECTROLYTIC SOLUTION III ELECTRICAL CONDUCTIVITY OF HEXAMMINE COBALT (III) SULPHATE AT HIGH PRESSURES

BY JIRO OSUGI, KIYOSHI SHIMIZU AND HIDETO TAKIZAWA

The degree of dissociation, α and dissociation constant, K of $[Co(NH_3)_6](SO_4)^+$ have been determined from the equivalent conductivity, Λ, of the dilute solution ($1.0\times10^{-4}\sim8.0\times10^{-4}$N) of $[Co(NH_3)_6]_2(SO_4)_3$ at 25~40°C under high pressures up to 600 kg/cm^2. Λ, α and K increase with increasing pressure. The entropy change for dissociation, ΔS is negative and becomes less negative with increasing pressure and temperature. The volume change, ΔV is negative and becomes more negative with increasing pressure at 25 and 30°C and less negative at 40°C. These phenomena have been explained with the properties of solvated water under high pressure. The increase of Λ with pressure is mainly ascribed to the increase of the ionic mobility at 25 and 30°C, and the increase of the degree of dissociation at 40°C; the ionic mobility decreases with pressure at this temperature.

Introduction

In the previous papers, the authors reported the effect of pressure on the dissociation of ion-pair by measuring the equivalent conductivity of an aqueous solution of hexammine cobalt (III) chloride under high pressures[1] and discussed on the mechanism of migration of free ion in water by the theory of transition state[2].

Now, the authors have studied the ionic conductivity of the aqueous solution of a complex salt, $[Co(NH_3)_6]_2(SO_4)_3$, at 25~40°C up to 600 kg/cm^2 and examined the pressure and temperature effects on the degree of dissociation, α, and the dissociation constant, K, of $[Co(NH_3)_6](SO_4)^+$ to $[Co(NH_3)_6]^{3+}$ and SO_4^{2-}.

Experimentals

Hexammine cobalt (III) sulphate, $[Co(NH_3)_6]_2(SO_4)_3$, was prepared from the water solution of cobaltous sulphate, ammonia, ammonium sulphate and decolorizing charcoal as a catalyst by the method

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1) K. Shimizu, H. Takizawa and J. Osugi, *This Journal*, 33, 1 (1963)

2) J. Osugi, K. Shimizu and H. Takizawa, *ibid.*, 34, 55 (1964)

of Bjerrum and McReynolds[3]. The crystals were thoroughly washed with conductivity water and absolute alcohol, then dried at 150～180°C till constant weight was attained as the result of complete dehydration[4]. As described in the previous paper[1], the high pressure conductivity cell made of teflon, of capacity 25 m*l* and cell constant 0.322 cm^{-1}, was mounted in a high pressure vessel containing a thermocouple of chromel-alumel. The solution, which was isolated with mercury in a glass cup from a silicone oil, was compressed by an oil injector. The conductivity was measured at concentrations of solution 1.0×10^{-4}～8.0×10^{-4} N in the temperature range of 25～40°C up to 600 kg/cm^2. In order to calculate the equivalent conductivity of solution under high pressures, it is necessary to know their compressibility. No such data are available for the hexammine cobalt (III) sulphate solution and thus the calculations were made in terms of the compressibility of water[5].

Results and Considerations

The equivalent conductivity, Λ, increases with increasing pressure as shown in Fig. 1 and shown later in Table 1. The increments of Λ with pressure decrease with rising temperature and decreasing concentration of solution. As the equivalent conductivity is proportional to the degree of ionization and the ionic mobilities, the effects of pressure on the degree of ionization and ionic mobility should be examined. The equivalent conductivity at infinite dilution, Λ_0, is given by the extrapolation of the plots of Λ against the square root of equivalent concentration, $C^{\frac{1}{2}}$, to zero concentration and the theoretical

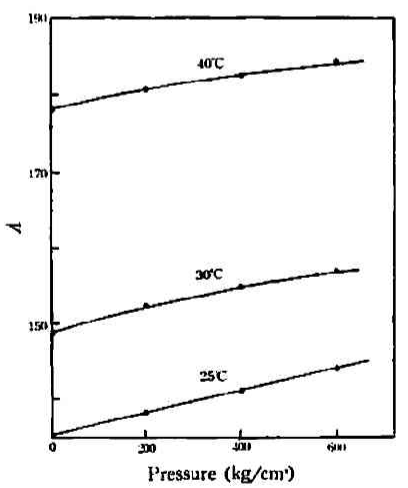

Fig. 1 Pressure dependence of equivalent conductivity of $[Co(NH_3)_6]_2(SO_4)_3$ solution

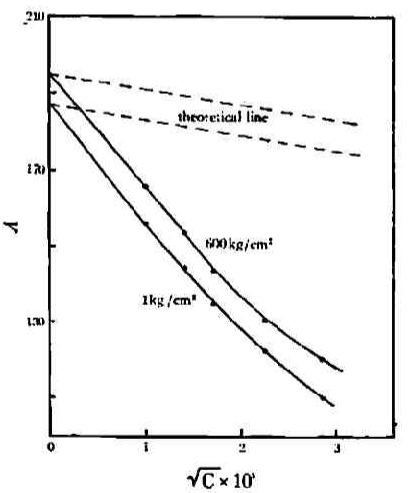

Fig. 2 Equivalent conductivity of $[Co(NH_3)_6]_2(SO_4)_3$ solution at two pressures

3) W. C. Fernelius, "Inorganic Syntheses", II, p. 216, McGraw-Hill (1946)
4) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", XIV, p. 790, Longmans Green & Co. (1935)
5) R. E. Gibson and O. H. Loeffler, *J. Am. Chem. Soc.*, **63**, 898 (1941)

equation of Onsager is obtained. Fig. 2 shows the plots of Λ against $C^{\frac{1}{2}}$ at 25°C, 1 and 600 kg/cm². The experimental conductivity curves lie below Onsager's theoretical lines. This difference may be attributed to the ion-pair $[Co(NH_3)_6](SO_4)^+$ formed between $[Co(NH_3)_6]^{3+}$ ion and SO_4^{2-} ion as pointed out by Linhard and Monk[6]. Then, the ion-pair, $[Co(NH_3)_6](SO_4)^+$, would be in equilibrium with $[Co(NH_3)_6]^{3+}$ and SO_4^{2-} ions :

$$\underset{2(1-\alpha)m}{[Co(NH_3)_6](SO_4)^+} \rightleftharpoons \underset{2\alpha m}{[Co(NH_3)_6]^{3+}} + \underset{(2\alpha+1)m}{SO_4^{2-}}, \qquad (1)$$

where α is the degree of dissociation and m is the molar concentration of hexammine cobalt (III) sulphate. The equivalent conductivity is as follows,

$$\Lambda C = 10^3\kappa = \sum_i z_i m_i \lambda \qquad (2)$$

and $C=6m$, where κ is the solvent-corrected specific conductivity, m_i the concentration (g ion/l) of z_i-valent ion i and λ_i its ionic conductivity.

Then,

$$\Lambda = \alpha[\lambda_{[Co(NH_3)_6]^{3+}} + \lambda_{SO_4^{2-}}] + \frac{(1-\alpha)}{3}[\lambda_{[Co(NH_3)_6](SO_4)^+} + \lambda_{SO_4^{2-}}],$$

$$\therefore \quad \Lambda = \alpha\Lambda^{32} + \frac{(1-\alpha)}{3}\Lambda^{12}$$

$$= \alpha\left\{(\Lambda_0^{32} - \frac{1}{3}\Lambda_0^{12}) - (b^{32} - \frac{1}{3}b^{12})I^{\frac{1}{2}}\right\} + \frac{1}{3}(\Lambda_0^{12} - b^{12}I^{\frac{1}{2}}) \qquad (3)$$

where

$$\lambda_{[Co(NH_3)_6]^{3+}} + \lambda_{SO_4^{2-}} = \Lambda^{32} = \Lambda_0^{32} - b^{32}I^{\frac{1}{2}},$$

$$\lambda_{[Co(NH_3)_6](SO_4)^+} + \lambda_{SO_4^{2-}} = \Lambda^{12} = \Lambda_0^{12} - b^{12}I^{\frac{1}{2}}$$

and ionic strength, I, is equal to $\frac{1}{2}(4\alpha+1)C$. In this case, the ionic mobility of the monovalent ion-pair is taken as one-third of that of the tervalent cation. The degree of dissociation, α, is obtained from the experimental values of Λ under pressure and Eq. (3) by means of successive approximation. In Eq. (3), the term b is the function of the viscosity of the solvent and the dielectric constant, of which the values of Bridgman[7] and Owen[8] were used respectively in this calculation.

The dissociation constant, K, is represented by the following equation,

$$K = \frac{\{[Co(NH_3)_6]^{3+}\}\{SO_4^{2-}\}}{\{[Co(NH_3)_6](SO_4)^+\}} = \frac{\alpha(1+2\alpha)C}{6(1-\alpha)} \cdot \frac{f_1 \cdot f_2}{f_3} \qquad (4)$$

where f_i ($i=1, 2, 3$) are the activity coefficients of $[Co(NH_3)_6]^{3+}$, SO_4^{2-} and $[Co(NH_3)_6](SO_4)^+$ ions, which are calculated from the Debye-Hückel equation,

$$-\log f_i = (1.825\times10^6 \cdot z_i^2 \cdot I^{\frac{1}{2}})/(\varepsilon T)^{\frac{3}{2}}.$$

Now, ΔG due to the dissociation reaction in Eq. (1) is related to the equilibrium constant K by the thermodynamic equation of $\Delta G = -RT\ln K$.

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6) V. M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944)
I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, 68 (1951)

7) P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **61**, 57 (1926)

8) B. B. Owen, R. C. Miller, C. E. Milner and H. L. Cogan, *J. Phys. Chem.*, **65**, 2065 (1961)

Then, the change of entropy, ΔS, in obtained as follows,

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P = R\ln K + RT\left(\frac{\partial \ln K}{\partial T}\right)_P \qquad (5)$$

On the other hand, the pressure coefficient of $\ln K$ gives the volume change, ΔV, due to the dissociation according to the thermodynamic relation as follows,

$$\Delta V = \left(\frac{\partial \Delta G}{\partial P}\right)_T = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T \qquad (6)$$

These results are summarized in Tables 1, 2 and Figs. 3 and 4. The degree of dissociation of each solution increases with increasing pressure and decreases with rising temperature. As shown in Table 2 and Fig. 3, the equilibrium constant, K, has the minimum value in the temperature range of 30~40°C, and increases with increasing pressure. ΔS in this system becomes less negative with increasing pressure and temperature. On the other hand, the volume change, ΔV, for the dissociation becomes more negative with increasing pressure at 25 and 30°C, but at 40°C less negative with increasing pressure (Fig. 4).

In a discussion of the thermodynamic quantities in the system of ionic solution, two effects must be considered: the changes in the thermodynamic quantities of the ions themselves, and changes of the

Table 1 Λ_0, and α under pressures

25°C

P (kg/cm²)	Λ_0	1×10^{-4}N		2×10^{-4}N		3×10^{-4}N		5×10^{-4}N		8×10^{-4}N	
		Λ	α	Λ	α	Λ	α	Λ	α	Λ	α
1	187.0	157.4	0.835	144.6	0.757	135.4	0.698	122.6	0.619	110.5	0.543
200	191.5	161.4	0.836	148.5	0.759	138.3	0.701	125.7	0.622	114.0	0.548
400	194.1	163.8	0.837	151.0	0.763	141.2	0.706	128.5	0.627	117.3	0.558
600	195.0	165.5	0.843	153.3	0.773	143.9	0.716	131.2	0.642	119.8	0.575

30°C

P (kg/cm²)	Λ_0	1×10^{-4}N		2×10^{-4}N		3×10^{-4}N		5×10^{-4}N		8×10^{-4}N	
		Λ	α	Λ	α	Λ	α	Λ	α	Λ	α
1	208.4	174.0	0.826	159.9	0.750	149.0	0.689	133.5	0.599	120.2	0.523
200	212.8	177.7	0.826	163.4	0.750	152.4	0.690	137.2	0.604	124.0	0.531
400	214.5	180.1	0.830	166.0	0.755	155.2	0.695	140.6	0.614	127.7	0.545
600	215.8	181.9	0.838	168.0	0.767	157.2	0.708	142.8	0.630	130.8	0.565

40°C

P (kg/cm²)	Λ_0	1×10^{-4}N		2×10^{-4}N		3×10^{-4}N		5×10^{-4}N		8×10^{-4}N	
		Λ	α	Λ	α	Λ	α	Λ	α	Λ	α
1	253.0	209.6	0.819	192.0	0.740	178.5	0.677	161.1	0.596	146.8	0.531
200	250.4	209.8	0.831	193.0	0.756	180.7	0.699	164.5	0.624	150.9	0.563
400	248.7	210.6	0.842	194.6	0.771	182.7	0.716	167.2	0.645	154.2	0.587
600	246.3	210.4	0.852	195.8	0.788	184.6	0.737	169.6	0.668	156.4	0.608

Table 2 K, ΔS and ΔV for dissociation of ion-pair $[Co(NH_3)_6](SO_4)^+$

	T(°C)	P(kg/cm²)			
		1	200	400	600
$K\cdot10^4$ (mole/l)	25	1.95	2.00	2.09	2.26
	30	1.81	1.86	1.96	2.18
	40	1.74	1.99	2.23	2.51
ΔS (e. u.)	25	−31	−29	−28	−26
	30	−24	−22	−18	−16
	40	−15	− 5.0	− 0.6	1.5
ΔV (cm³/l)	25	− 2.0	− 4.5	− 7.4	−12
	30	− 2.6	− 4.9	− 9.2	−17
	40	−20	−17	−15	−13

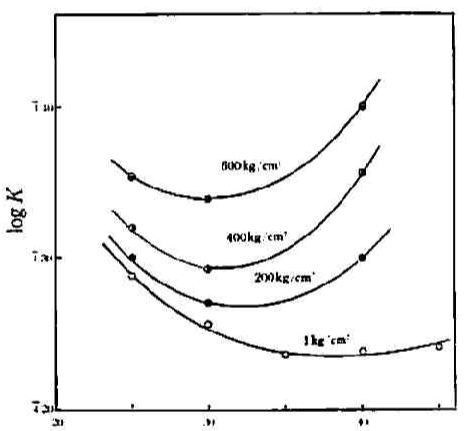

Fig. 3 Temperature dependence of dissociation constant of $[Co(NH_3)_6]_2(SO_4)_3$ solution

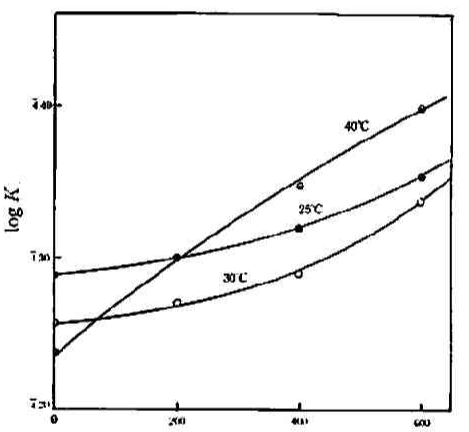

Fig. 4 Pressure dependence of dissociation constant of $[Co(NH_3)_6]_2(SO_4)_3$ solution

quantities in the neighbouring molecules, or the interaction between ions and solvent molecules. Namely, $\Delta S=\Delta S_1+\Delta S_2$ and $\Delta V=\Delta V_1+\Delta V_2$, where suffix 1 denotes the changes of the ions themselves and suffix 2 the changes due to the ion-solvent molecules interactions. In the dissociation of $[Co(NH_3)_6](SO_4)^+$ to $[Co(NH_3)_6]^{3+}$ and SO_4^{2-}, it is reasonable to consider ΔS_1 and ΔV_1 to be positive. On the other hand, ΔS and ΔV in this system are negative as shown in Table 2 so that the ΔS_2 and ΔV_2 are negative and $|\Delta S_2|$ and $|\Delta V_2|$ should be larger than $|\Delta S_1|$ and $|\Delta V_1|$, respectively. According to the electrostatic theory, these effects would be ascribed to the enhancement of the solvation of the free ions due to the increase of the ionic charges in the dissociation reaction from $[Co(NH_3)_6](SO_4)^+$ to $[Co(NH_3)_6]^{3+}$ and SO_4^{2-}. Under high pressure, the dielectric constant of water increases with increasing pressure, with consequent decrease of the free energy of solution leading to a more negative value of ΔV and a less negative valus of ΔS.

Now, we must keep in mind the special properties of water as a solvent. especially an ice-like

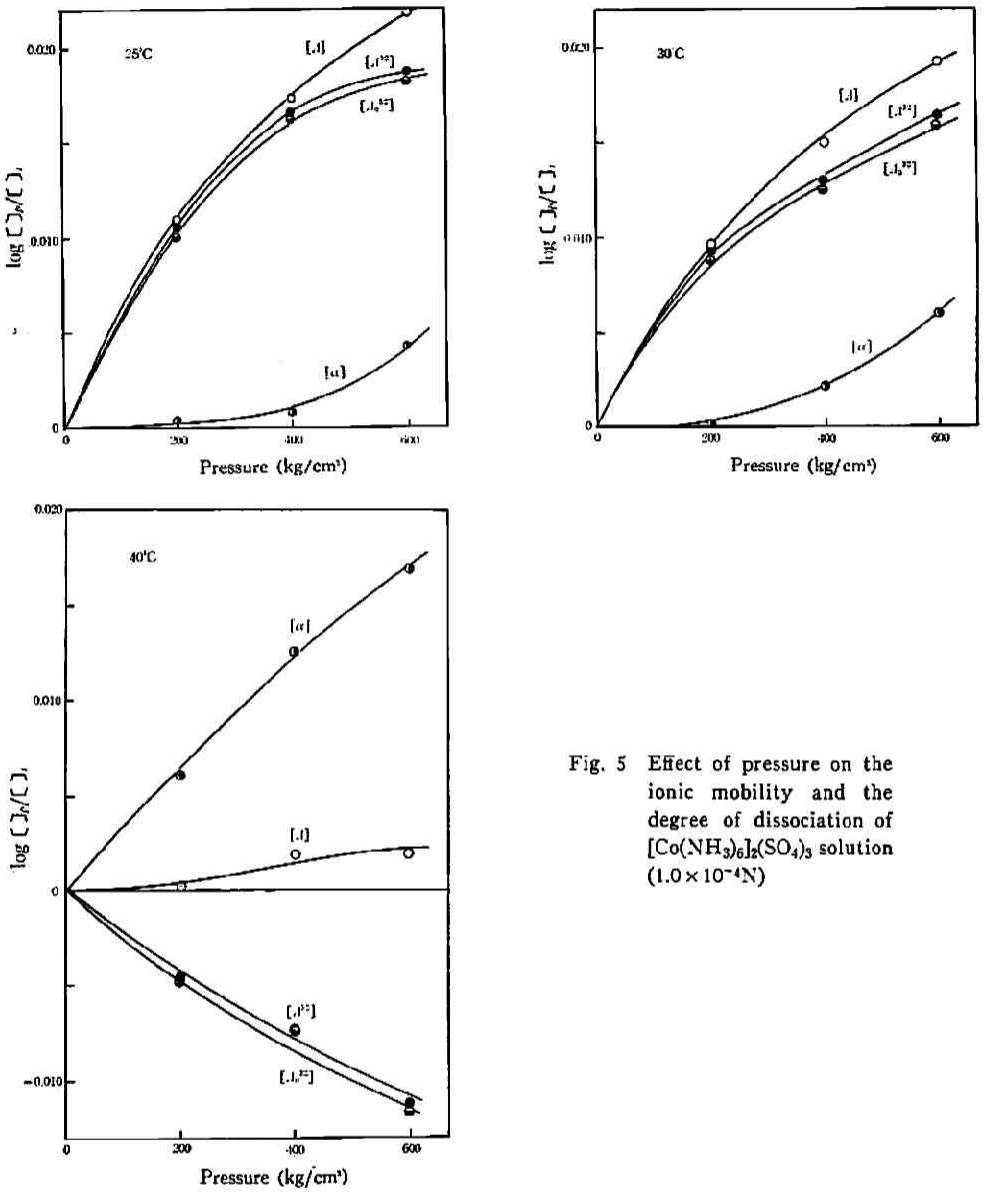

Fig. 5 Effect of pressure on the ionic mobility and the degree of dissociation of $[Co(NH_3)_6]_2(SO_4)_3$ solution (1.0×10^{-4}N)

structure. In the aqueous solution, the electric field is very strong in the neighbourhood of the solute ion, so that the nearest-neighbour water molecules are oriented appropriately to the ion and immobilized by direct ion-dipole interaction. The normal water molecules as a continuous matrix would be polarized and in the ordinary way by the ionic field which has become relatively weak. Then, the two competing orienting influences would make the water molecules in the intermediate region between the innermost region and the continuous matrix have a collapsed structure (less ice-like), or more random in organization[9].

9) R. W. Gurney, "Ionic Processes in Solution", p. 248, McGraw-Hill (1953)

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The balances in the three regions would affect ΔS and ΔV, and the variation of ΔS and ΔV with temperature and pressure may be mainly ascribed to the increase of the intermediate region (collapsed structure) as compared with the other two regions of the solvated water molecules as mentioned above. At higher temperatures, the ice-like structure of water may be somewhat broken down as deduced by the increase of viscosity of water with increasing pressure, and the effect of pressure on ΔV would go in reverse at 40°C.

It is interesting to examine the effects of pressure on the equivalent conductivity and the mobility of ions. The equivalent conductivity, Λ, is mainly contributed by free ions of $[Co(NH_3)_6]^{3+}$ and SO_4^{2-} so that we can postulate from Eq. (3) that $\Lambda \fallingdotseq \alpha\Lambda^{32} \sim \alpha\Lambda_0^{32}$.

$$\therefore \quad \ln\frac{[\Lambda]_P}{[\Lambda]_1} \fallingdotseq \ln\frac{[\alpha]_P}{[\alpha]_1} + \ln\frac{[\Lambda^{32}]_P}{[\Lambda^{32}]_1} \sim \ln\frac{[\alpha]_P}{[\alpha]_1} + \ln\frac{[\Lambda_0^{32}]_P}{[\Lambda_0^{32}]_1}. \tag{7}$$

The changes of $\ln[\Lambda]_P/[\Lambda]_1$, $\ln[\alpha]_P/[\alpha]_1$, $\ln[\Lambda^{32}]_P/[\Lambda^{32}]_1$ and $\ln[\Lambda_0^{32}]_P/[\Lambda_0^{32}]_1$ with pressure are shown in Fig 5. The increase of Λ with pressure at 25 and 30°C would be due to the increase of Λ_0, that is the increase of mobility of ion, with pressure rather than to the degree of dissociation, α. But, at 40°C the increase of Λ with pressure would depend on the increase of α with pressure and the Λ_0 and the mobility of ion decrease with increasing pressure. These phenomena may be ascribed to the properties of solvent water under high pressure and accord with the variation of the viscosity of water with pressure and temperature.

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